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(54) **COMPOSITIONS COMPRISING 1,1-DIFLUOROETHENE, TRIFLUOROMETHANE AND A THIRD COMPONENT**

ZUSAMMENSETZUNGEN AUS 1,1-DIFLUORETHAN, TRIFLUORETHAN UND EINE DRITTE KOMPONENTE

COMPOSITIONS DE 1,1-DIFLUOROETHENE, TRIFLUOROMETHANE ET UN TROISIÈME COMPOSANT

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**WO-A1-2014/134821 WO-A1-2014/156190**  
**WO-A1-2015/015188 WO-A1-2015/147338**  
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**Description**

**[0001]** The invention relates to compositions, preferably to heat transfer compositions, and in particular to ultra-low temperature heat transfer compositions which may be suitable as replacements for existing refrigerants such as R-508A, R-508B, R-23 or R-13B1.

**[0002]** The listing or discussion of a prior-published document or any background in the specification should not necessarily be taken as an acknowledgement that a document or background is part of the state of the art or is common general knowledge.

**[0003]** Mechanical refrigeration systems and related heat transfer devices such as heat pumps and air-conditioning systems are well known. In such systems, a refrigerant liquid evaporates at low pressure taking heat from the surrounding zone. The resulting vapour is then compressed and passed to a condenser where it condenses and gives off heat to a second zone, the condensate being returned through an expansion valve to the evaporator, so completing the cycle. Mechanical energy required for compressing the vapour and pumping the liquid is provided by, for example, an electric motor or an internal combustion engine.

**[0004]** Certain refrigerant applications, notably biomedical refrigeration, use low-boiling refrigerant gases to achieve cooling of materials, typically to temperatures of about -85 °C or below. These fluids are sometimes referred to as ultra-low temperature (ULT) or cryogenic refrigerants.

**[0005]** The most commonly used non-flammable ULT refrigerants currently are R-508A and R-508B. The term R-508 is used herein to refer to R-508A and R-508B, which are both mixtures of trifluoromethane (R-23) with hexafluoroethane (R-116) and are rated A1 by the ASHRAE Standard 34 classification.

**[0006]** Typical low-temperature applications of R-508 fluids are normally cascade systems: a first vapour compression refrigeration cycle cools air inside a refrigerated compartment to between about -80 and -95°C by evaporation of liquid R-508. The gaseous refrigerant is then compressed and condensed in a heat exchanger, where it vaporises a second refrigerant (for example R-404A). A typical condensing temperature for R-508 in this exchanger is in the range -50 to -30°C, typically about 40 °C. The second refrigerant vapour is compressed by a second compressor and is then condensed against ambient air.

**[0007]** The greenhouse (or global) warming potential (GWP) of low boiling non-flammable refrigerant gases such as R-508 or R-23 is high (e.g. about 13000), and it is desired to find fluids able to be used in this application with lower GWP, so as to reduce the environmental impact of refrigerant leakage.

**[0008]** In looking for alternative low temperature refrigerants several other factors must also be considered. Firstly, if the fluid is to be used as a retrofit or conversion fluid in existing equipment, or as a "drop-in" to new equipment using an essentially unchanged R-508 system design, then non-flammability is highly desired, as the existing design will have been based on the use of non-flammable fluid.

**[0009]** If an alternative fluid is to be employed in a wholly new system design then a degree of flammability may be tolerable; but the use of highly flammable fluids may impose cost and performance penalties to mitigate hazards. Acceptable charge size (refrigerant mass) in a system is also governed by the flammability classification of the fluid, with class 3 fluids, such as ethane, being the most strictly limited. In this case a weaker flammability characteristic is highly desirable since it may allow larger system charges.

**[0010]** Thirdly, the typical application of such fluids is in commercial or laboratory based equipment and so the systems will be located in buildings. It is therefore desirable to have acceptably low toxicity as a characteristic of the fluid.

**[0011]** Furthermore, the volumetric capacity (a measure of the cooling power achievable by a given size of compressor) and energy efficiency are important. This is especially so in cascade operation as inefficiency in the low temperature stage also increases power consumption of the compressor in the top stage of the cascade.

**[0012]** R-170 (ethane) has very low GWP, acceptable refrigeration performance and toxicity but its high flammability limits its application: for example safety regulations can restrict the maximum charge quantity of refrigerant in appliances.

**[0013]** Binary mixtures of R-170 with R-116 have been described by Zhang et al. (J Chem Eng Data 2005 50 2074-2076 and Fluid Phase Equilibria 2006 240 73-78). They identified an azeotropic binary composition of these two components.

**[0014]** R-744 (carbon dioxide) is non-flammable but cannot be used alone in the bottom stage of ULT cascade systems because the operating temperatures are below the triple point of R-744. This means that solid carbon dioxide (dry-ice) could form in low pressure sections of the system, leading to blockages, poor control and inefficient operation.

**[0015]** Binary mixtures of R-744 with R-116 have been described by Valtz et al (Fluid Phase Equilibria 258 (2007) 179-185). They identified an azeotropic binary composition of these two components.

WO2014/134821 relates to compositions, methods and systems having utility particularly in refrigeration applications. WO2014/156190 relates to a binary refrigerating apparatus using a mixed refrigerant. CN101434831 relates to the field of cooling by using a cascade system, in particular to a low-temperature mixing working medium of a cascade refrigeration system containing N<sub>2</sub>O (R744A).

WO2015/147338 relates to a binary refrigerating apparatus using a mixed refrigerant.

WO2015/015188 relates to compositions, preferably to heat transfer compositions, and in particular to ultra-low temper-

ature heat transfer compositions.

R-1132a (1,1-difluoroethene, also known as vinylidene fluoride) also has low GWP and acceptable toxicity. The flammability of R-1132a is reduced compared to ethane but it is still in flammability class 2. US6054064 describes the use of R-1132a in certain refrigerant compositions including mixtures with R-23, R-32, R-125, R-134a and R-143a. The thermodynamic energy efficiency of pure R-1132a is close to that of R-508 but its refrigeration capacity is reduced.

**[0016]** Thus there is a need to provide alternative refrigerants having improved properties such as low GWP, yet possessing acceptable refrigeration performance, flammability characteristics and toxicology. There is also a need to provide alternative refrigerants that may be used in existing devices such as refrigeration devices with little or no modification.

**[0017]** The subject invention addresses the above and other deficiencies by the provision of a composition comprising 1,1-difluoroethene (vinylidene fluoride, R-1132a), trifluoromethane and 1% by weight to 45% by weight carbon dioxide (R-744, CO<sub>2</sub>).

**[0018]** Also provided is the use of the compositions of the invention as refrigerants, preferably ultra-low temperature refrigerants. The ultra-low temperatures reached by the compositions of the invention may be -70 °C or below, such as -80 °C or below, preferably -85 °C or below, or even -90 °C or below.

**[0019]** Surprisingly, it has been found that the compositions of the invention exhibit further enhanced refrigeration capacities compared to R-23 and reduced flammability compared to R-1132a.

**[0020]** The invention is as defined in the claims.

**[0021]** The compositions of the invention may contain about 15% by weight or less of carbon dioxide, such as about 10% by weight or less carbon dioxide.

**[0022]** Advantageously, compositions of the invention may comprise from about 1 to about 98% by weight R-1132a and/or from about 1 to about 98% by weight R-23.

**[0023]** Preferably the compositions may contain from about 35 to about 95% by weight R-1132a, such as from about 35 to about 90% by weight, from about 35 to about 85% by weight R-1132a, or from about 37 to about 80% by weight R-1132. Even more preferably the compositions may comprise from about 40 to about 60% by weight R-1132a. Advantageously, compositions may contain from about 1 to about 90% by weight R-23, such as from about 1 to about 75% by weight R-23, e.g. from about 60 to about 70% by weight R-23 or from about 1 to about 40% by weight R-23. Composition of the invention may contain from about 1 to about 30% by weight R-23, such as from about 1 to about 25% by weight R-23 or from about 5 to about 25% by weight R-23, from about 7 to about 22% by weight R-23 or from about 1 to about 20% by weight R-23. the invention, the composition contains from about 1 to about 45% by weight carbon dioxide, such as from about 1 to about 35% by weight carbon dioxide, preferably from about 1 to about 30% by weight carbon dioxide, even more preferably from about 1 to about 15% by weight carbon dioxide, or even from about 1 to about 10% by weight carbon dioxide.

**[0024]** Preferably, compositions comprise from about 35 to about 95% by weight R-1132a, from about 1 to about 75% by weight R-23, from about 1 to about 60% by weight R-116 and from about 1 to about 35% by weight carbon dioxide.

**[0025]** Advantageously, compositions comprise from about 30 to about 85% by weight R-1132a, from about 1 to about 40% by weight R-23 and from about 1 to about 15% by weight carbon dioxide.

**[0026]** Preferably, compositions comprise from about 40 to about 70% by weight R-1132a, from about 1 to about 30% by weight R-23 and from about 1 to about 10% by weight carbon dioxide; such as from about 45 to about 70% by weight R-1132a, from about 1 to about 25% by weight R-23 and from about 1 to about 7% by weight carbon dioxide, or even from about 45 to about 70% by weight R-1132a, from about 1 to about 25% by weight R-23 and from about 1 to about 5% by weight carbon dioxide.

**[0027]** In an embodiment, the composition of invention comprise both R-116 and R-170. Preferably, the composition comprises R-116 and R-170 in the amounts specified above. In an embodiment, the compositions may contain from about 35 to about 95% by weight R-1132a, from about 1 to about 75% by weight R-23, from about 1 to about 50% by weight R-116 and from about 1 to about 40% by weight R-170.

**[0028]** Preferably, the compositions comprise from about 35 to about 70% by weight R-1132a, from about 1 to about 40% by weight R-23, from about 1 to about 40% by weight R-116 and from about 1 to about 30% by weight R-170; such as from about 40 to about 70% by weight R-1132a, from about 1 to about 30% by weight R-23, from about 1 to about 30% by weight R-116 and from about 1 to about 15% by weight R-170.

**[0029]** In an embodiment, the compositions comprise from about 35 to about 95% by weight R-1132a, from about 1 to about 75% by weight R-23, from about 1 to about 50% by weight R-116 and from about 1 to about 40% by weight carbon dioxide.

**[0030]** Preferably, the compositions comprise from about 35 to about 70% by weight R-1132a, from about 1 to about 40% by weight R-23, from about 1 to about 40% by weight R-116 and from about 1 to about 15% by weight carbon dioxide; such as from about 40 to about 70% by weight R-1132a, from about 1 to about 30% by weight R-23, from about 1 to about 30% by weight R-116 and from about 1 to about 10% by weight R-170.

**[0031]** In an embodiment, the compositions comprise from about 35 to about 95% by weight R-1132a, from about 1

to about 75% by weight R-23, from about 1 to about 30% by weight R-170 and from about 1 to about 40% by weight carbon dioxide.

[0032] Preferably, the compositions comprise from about 35 to about 70% by weight R-1132a, from about 1 to about 40% by weight R-23, from about 1 to about 20% by weight R-170 and from about 1 to about 15% by weight carbon dioxide.

[0033] Preferably, the compositions comprise from about 40 to about 70% by weight R-1132a, from about 1 to about 30% by weight R-23, from about 1 to about 10% by weight R-170 and from about 1 to about 10% by weight R-170.

[0034] In an embodiment, the composition comprises R-1132a, R-23, R-116, R-170 and carbon dioxide.

[0035] In some instances, wherein the composition does not additionally comprise hexafluoroethane (R-116), the composition comprises about 1 to about 98% by weight R-1132a about 1 to about 98% by weight R-23 and about 1 to about 50% by weight carbon dioxide. For example, in some embodiments the composition may comprise about 35 to 98% by weight R-1132a, about 1 to about 60% by weight R-23 and about 1 to about 20% by weight carbon dioxide. In some of these embodiments, the composition may comprise about 40 to about 60% by weight R-23, for example about 45 to about 55% by weight R23. It is preferred that any of such compositions comprise about 4 to about 16% by weight carbon dioxide.

[0036] Any of the above described compositions may further contain a hydrocarbon, wherein the hydrocarbon is in addition to any ethane present in the composition. Advantageously, the hydrocarbon is one or more compound(s) selected from the group consisting of propane, propene, isobutane, n-butane, n-pentane, isopentane and mixtures thereof. In a preferred embodiment, the hydrocarbon comprises n-pentane.

[0037] Without being bound by theory, it is believed that, when present, the inclusion of ethane and/or an additional hydrocarbon compound may enhance oil miscibility, solubility and/or return characteristics. Preferably, the compositions of the invention preferably contain from about 1 to about 50% by weight of the hydrocarbon component, for example from about 1 to about 20%.

[0038] In an embodiment, the compositions may consist essentially of the stated components.

[0039] By the term "consist essentially of", we mean that the compositions of the invention contain substantially no other components, particularly no further (hydro)(fluoro)compounds (e.g. (hydro)(fluoro)alkanes or (hydro)(fluoro)alkenes) known to be used in heat transfer compositions. The term "consist of" is included within the meaning of "consist essentially of".

[0040] In an embodiment, the compositions of the invention are substantially free of any component that has heat transfer properties (other than the components specified). For instance, the compositions of the invention may be substantially free of any other hydrofluorocarbon compound.

[0041] By "substantially no" and "substantially free of", we include the meaning that the compositions of the invention contain 0.5% by weight or less of the stated component, preferably 0.1% or less, based on the total weight of the composition.

[0042] The compositions of the invention may be azeotropic.

[0043] By azeotropic composition, we include the meaning of a composition which at vapour-liquid equilibrium has the same composition in both phases, and whose boiling point is lower than that of the pure components. All the azeotropic compositions of the invention have been found to exhibit a positive deviation from ideality. By near-azeotropic composition we include the meaning of liquid compositions whose vapour pressure is above that of the pure component with the lower boiling point when measured at equivalent temperature, but whose equilibrium vapour composition may differ from the liquid composition.

[0044] All of the chemicals herein described are commercially available. For example, the fluorochemicals may be obtained from Apollo Scientific (UK) and carbon dioxide may be obtained from liquefied gas suppliers such as Linde AG.

[0045] As used herein, all % amounts mentioned in compositions herein, including in the claims, are by weight based on the total weight of the compositions, unless otherwise stated.

[0046] By the term "about", as used in connection with numerical values of amounts of components in % by weight, we include the meaning of  $\pm 0.5$  % by weight, for example  $\pm 0.2$  % by weight or  $\pm 0.1$  % by weight.

[0047] For the avoidance of doubt, it is to be understood that the stated upper and lower values for ranges of amounts of components in the compositions of the invention described herein may be interchanged in any way, provided that the resulting ranges fall within the broadest scope of the invention.

[0048] The compositions of the invention have zero ozone depletion potential

[0049] Typically, the compositions of the invention have a GWP of less than about 12000, such as less than about 11000.

[0050] In one embodiment, the compositions of the invention have a GWP of less than about 11000, preferably less than about 10500 or about 10000 or about 9000 or about 8000.

[0051] In one aspect, the compositions of the invention comprising R-1132a, R-116 and R-23 have a GWP of less than about 11000, for instance less than about 10000, e.g. from about 100 to about 10000, or from about 100 to about 7000

[0052] In one embodiment, the compositions of the invention comprising R-1132a, R-23, R-116 and CO<sub>2</sub> have a GWP of less than about 10000, for instance less than about 9000, e.g. from about 1000 to about 8000, or from about 2000 to about 7000.

**[0053]** Typically, the compositions of the subject invention are of reduced flammability hazard when compared to R-1132a.

**[0054]** Flammability may be determined in accordance with ASHRAE Standard 34 incorporating the ASTM Standard E-681 with test methodology as per Addendum 34p dated 2004, the entire content of which is incorporated herein by reference.

**[0055]** In some embodiments, the compositions have one or more of (a) a higher lower flammable limit; (b) a higher ignition energy (sometimes referred to as auto ignition energy or pyrolysis); or (c) a lower flame velocity compared to R-1132a alone. Preferably, the compositions of the invention are less flammable compared to R-1132a in one or more of the following respects: lower flammable limit at 23°C; lower flammable limit at 60°C; breadth of flammable range at 23°C or 60°C; auto-ignition temperature (thermal decomposition temperature); minimum ignition energy in dry air or flame speed. The flammable limits being determined according to the methods specified in ASHRAE-34 and the auto-ignition temperature being determined in a 500ml glass flask by the method of ASTM E659-78.

**[0056]** In a preferred embodiment, the compositions of the invention are non-flammable. For example, the compositions of the invention are non-flammable at a test temperature of 60°C using the ASHRAE-34 methodology. Advantageously, the mixtures of vapour that exist in equilibrium with the compositions of the invention at any temperature between about-20°C and 60°C are also non-flammable.

**[0057]** In some applications it may not be necessary for the formulation to be classed as non-flammable by the ASHRAE-34 methodology; it is possible to develop fluids whose flammability limits will be sufficiently reduced in air to render them safe for use in the application, for example if it is physically not possible to make a flammable mixture by leaking the refrigeration equipment charge into the surrounds.

**[0058]** In one embodiment, the compositions of the invention have a flammability classifiable as 1 or 2L according to the ASHRAE standard 34 classification method, indicating non-flammability (class 1) or a weakly flammable fluid with flame speed lower than 10 cm/s (class 2L).

**[0059]** A composition of the invention preferably have a temperature glide in an evaporator or condenser of less than about 10 K, even more preferably less than about 5 K, such as less than about 1 K.

**[0060]** The critical temperature of a heat transfer composition should be higher than the maximum expected condenser temperature. This is because the cycle efficiency drops as critical temperature is approached. As this happens, the latent heat of the refrigerant is reduced and so more of the heat rejection in the condenser takes place by cooling gaseous refrigerant; this requires more area per unit heat transferred. The critical temperature of R-508B is about 11 °C (data estimated by REFPROP).

**[0061]** In one aspect, the compositions of the invention have a critical temperature of greater than about 0 °C, preferably greater than about 10 °C

**[0062]** It is believed that the compositions of the invention exhibit a completely unexpected combination of low-/non-flammability, low GWP, improved lubricant miscibility and improved refrigeration performance properties. Some of these refrigeration performance properties are explained in more detail below.

**[0063]** The compositions of the invention typically have a volumetric refrigeration capacity that is at least 85% of that of R-508 at comparable cycle conditions. Preferably, the compositions of the invention have a volumetric refrigeration capacity that is at least 90% of that of R-508, for example from about 95% to about 120% of that of R-508.

**[0064]** The compositions of the invention typically are capable of reaching temperatures of -70 °C or lower, preferably -80 °C or lower, for example -85 °C or lower whilst maintaining the evaporation pressure above atmospheric pressure.

**[0065]** In one embodiment, the cycle efficiency (Coefficient of Performance, COP) of the compositions of the invention is within about 5% or even better than the existing refrigerant fluid it is replacing. Conveniently, the compressor discharge temperature of the compositions of the invention is within about 15 K of the existing refrigerant fluid it is replacing, preferably about 10 K or even about 5 K.

**[0066]** The compositions of the invention are typically suitable for use in existing designs of equipment, for example, ULT refrigeration equipment and are compatible with all classes of lubricant currently used with established HFC refrigerants. They may be optionally stabilised or compatibilised with mineral oils by the use of appropriate additives.

**[0067]** Preferably, when used in heat transfer equipment, the composition of the invention is combined with a lubricant.

**[0068]** Conveniently, the lubricant is selected from the group consisting of mineral oil, silicone oil, polyalkyl benzenes (PABs), polyol esters (POEs), polyalkylene glycols (PAGs), polyalkylene glycol esters (PAG esters), polyvinyl ethers (PVEs), poly (alpha-olefins) and combinations thereof. PAGs and POEs are currently preferred lubricants for the compositions of the invention.

**[0069]** Advantageously, the lubricant further comprises a stabiliser.

**[0070]** Preferably, the stabiliser is selected from the group consisting of diene-based compounds, phosphates, phenol compounds and epoxides, and mixtures thereof.

**[0071]** Conveniently, the composition of the invention may be combined with a flame retardant.

**[0072]** Advantageously, the flame retardant is selected from the group consisting of tri-(2-chloroethyl)-phosphate, (chloropropyl) phosphate, tri-(2,3-dibromopropyl)-phosphate, tri-(1,3-dichloropropyl)-phosphate, diammonium phos-

phate, various halogenated aromatic compounds, antimony oxide, aluminium trihydrate, polyvinyl chloride, a fluorinated iodocarbon, a fluorinated bromocarbon, trifluoro iodomethane, perfluoroalkyl amines, bromo-fluoroalkyl amines and mixtures thereof.

**[0073]** In one embodiment, the invention provides a heat transfer device comprising a composition of the invention.

**[0074]** Preferably, the heat transfer device is a refrigeration device.

**[0075]** Conveniently, the heat transfer device is an ultra-low temperature refrigeration system.

**[0076]** Advantageously, the heat transfer device contains a cascade system.

**[0077]** The invention also provides the use of a composition of the invention in a heat transfer device as herein described.

**[0078]** According to another aspect of the invention, there is provided a sprayable composition comprising a material to be sprayed and a propellant comprising a composition of the invention.

**[0079]** According to a further aspect of the invention, there is provided a method for cooling an article which comprises condensing a composition of the invention and thereafter evaporating said composition in the vicinity of the article to be cooled.

**[0080]** According to another aspect of the invention, there is provided a method for heating an article which comprises condensing a composition of the invention in the vicinity of the article to be heated and thereafter evaporating said composition.

**[0081]** According to a further aspect of the invention, there is provided a method for extracting a substance from biomass comprising contacting the biomass with a solvent comprising a composition of the invention, and separating the substance from the solvent.

**[0082]** According to another aspect of the invention, there is provided a method of cleaning an article comprising contacting the article with a solvent comprising a composition of the invention.

**[0083]** According to a further aspect of the invention, there is provided a method for extracting a material from an aqueous solution comprising contacting the aqueous solution with a solvent comprising a composition of the invention, and separating the material from the solvent.

**[0084]** According to another aspect of the invention, there is provided a method for extracting a material from a particulate solid matrix comprising contacting the particulate solid matrix with a solvent comprising a composition of the invention, and separating the material from the solvent.

**[0085]** According to a further aspect of the invention, there is provided a mechanical power generation device containing a composition of the invention.

**[0086]** Preferably, the mechanical power generation device is adapted to use a Rankine Cycle or modification thereof to generate work from heat.

**[0087]** According to another aspect of the invention, there is provided a method of retrofitting a heat transfer device comprising the step of removing an existing heat transfer fluid, and introducing a composition of the invention. Preferably, the heat transfer device is a refrigeration device, more preferably still the device is an ultra-low temperature refrigeration system. Preferably, the refrigeration system cools a compartment to less than about -70 °C, preferably less than about -80 °C, for example to less than -85 °C, or even less than -90 °C.

**[0088]** Advantageously, the method further comprises the step of obtaining an allocation of greenhouse gas (e.g. carbon dioxide) emission credit.

**[0089]** In accordance with the retrofitting method described above, an existing heat transfer fluid can be fully removed from the heat transfer device before introducing a composition of the invention. An existing heat transfer fluid can also be partially removed from a heat transfer device, followed by introducing a composition of the invention.

**[0090]** The compositions of the invention may also be prepared simply by mixing the R-1132a, R-23 (and further components such as R-116, R-170, R-744, hydrocarbons, a lubricant, a stabiliser or an additional flame retardant) in the desired proportions. The compositions can then be added to a heat transfer device (or used in any other way as defined herein).

**[0091]** In a further aspect of the invention, there is provided a method for reducing the environmental impact arising from operation of a product comprising an existing compound or composition, the method comprising replacing at least partially the existing compound or composition with a composition of the invention. Preferably, this method comprises the step of obtaining an allocation of greenhouse gas emission credit.

**[0092]** By environmental impact we include the generation and emission of greenhouse warming gases through operation of the product.

**[0093]** As mentioned above, this environmental impact can be considered as including not only those emissions of compounds or compositions having a significant environmental impact from leakage or other losses, but also including the emission of carbon dioxide arising from the energy consumed by the device over its working life. Such environmental impact may be quantified by the measure known as Total Equivalent Warming Impact (TEWI). This measure has been used in quantification of the environmental impact of certain stationary refrigeration and air conditioning equipment, including for example supermarket refrigeration systems (see, for example, [http://en.wikipedia.org/wiki/Total\\_equivalent\\_warming\\_impact](http://en.wikipedia.org/wiki/Total_equivalent_warming_impact)).

**[0094]** The environmental impact may further be considered as including the emissions of greenhouse gases arising from the synthesis and manufacture of the compounds or compositions. In this case the manufacturing emissions are added to the energy consumption and direct loss effects to yield the measure known as Life-Cycle Carbon Production (LCCP, see for example <http://www.sae.org/events/aars/presentations/2007papasawa.pdf>). The use of LCCP is common

in assessing environmental impact of automotive air conditioning systems.

**[0095]** Emission credit(s) are awarded for reducing pollutant emissions that contribute to global warming and may, for example, be banked, traded or sold. They are conventionally expressed in the equivalent amount of carbon dioxide. Thus if the emission of 1 kg of R-134a is avoided then an emission credit of  $1 \times 1300 = 1300$  kg CO<sub>2</sub> equivalent may be awarded.

**[0096]** In another embodiment of the invention, there is provided a method for generating greenhouse gas emission credit(s) comprising (i) replacing an existing compound or composition with a composition of the invention, wherein the composition of the invention has a lower GWP than the existing compound or composition; and (ii) obtaining greenhouse gas emission credit for said replacing step.

**[0097]** In a preferred embodiment, the use of the composition of the invention results in the equipment having a lower Total Equivalent Warming Impact, and/or a lower Life-Cycle Carbon Production than that which would be attained by use of the existing compound or composition.

**[0098]** These methods may be carried out on any suitable product, for example in the fields of air-conditioning, refrigeration (e.g. low and medium temperature refrigeration), heat transfer, aerosols or sprayable propellants, gaseous dielectrics, flame suppression, solvents (e.g. carriers for flavorings and fragrances), cleaners, topical anesthetics, and expansion applications. Preferably, the field is ultra-low temperature refrigeration.

**[0099]** Examples of suitable products include heat transfer devices, sprayable compositions, solvents and mechanical power generation devices. In a preferred embodiment, the product is a heat transfer device, such as a refrigeration device or an ultra-low temperature refrigeration system.

**[0100]** The existing compound or composition has an environmental impact as measured by GWP and/or TEWI and/or LCCP that is higher than the composition of the invention which replaces it. The existing compound or composition may comprise a fluorocarbon compound, such as a perfluoro-, hydrofluoro-, chlorofluoro- or hydrochlorofluoro-carbon compound or it may comprise a fluorinated olefin.

**[0101]** Preferably, the existing compound or composition is a heat transfer compound or composition such as a refrigerant. Examples of refrigerants that may be replaced include ULT refrigerants such as R-508A, R-508B, R-23 and R-13B1.

**[0102]** Any amount of the existing compound or composition may be replaced so as to reduce the environmental impact. This may depend on the environmental impact of the existing compound or composition being replaced and the environmental impact of the replacement composition of the invention. Preferably, the existing compound or composition in the product is fully replaced by the composition of the invention.

**[0103]** The invention is illustrated by the following non-limiting examples, with reference to the following drawings:

Figure 1 shows a plot of R-23 concentration against capacity relative to R-508A for compositions of R-1132a, R-23 and carbon dioxide;

Figure 2 shows a plot of R-23 concentration against coefficient of performance relative to R-508A for compositions of R-1132a, R-23 and carbon dioxide.

## Examples

### [0104]

**Table 1: Cycle conditions for modelling ternary compositions**

Cycle conditions for modelling		
Condensing temperature	°C	-40
Evaporating temperature	°C	-85
Suction temperature	°C	same as evaporator outlet
Isentropic efficiency		65%
Subcooling	K	5
Evaporator superheat	K	5
Compressor clearance ratio		3%

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*Compositions of R-1132a, R23 and carbon dioxide*

**[0105]** The performance of ternary compositions of the invention are provided in the following Tables 15 to 18, which list performance characteristics for a range of ternary compositions. Plots of capacity and coefficient of performance of the compositions relative to R-508A against R-23 concentration are shown in Figures 1 and 2.

**[0106]** The cycle conditions used in the modelling are as Table 1.

Table 14 - Calculated performance of reference (r508b) and pure components

		R508A	R1132a	R23
Capacity relative to reference		100.0%	83.4%	79.3%
COP relative to reference		100.0%	94.2%	91.3%
Discharge temperature difference (K)		0.0	-3.8	46.1
Pressure ratio	-	7.71	6.74	8.35
Condenser glide	K	0.2	0.0	0.0
Evaporator glide	K	0.4	0.0	0.0
Condensing pressure	bar	8.53	7.01	7.06
Evaporating pressure	bar	1.11	1.04	0.85
COP	-	2.41	2.27	2.20
Discharge temperature	°C	11.4	7.6	57.5
Volumetric capacity	kJ/m3	935	780	742



Table 15

Quantity	Units												
		CO <sub>2</sub>	R23	R1132a	4%	4%	4%	4%	4%	4%	4%	4%	4%
Capacity relative to reference		86.2%	88.2%	89.8%	89.8%	90.8%	91.3%	91.2%	90.4%	88.9%	86.8%	84.1%	
COP relative to reference Discharge temperature difference (K)		94.1%	94.0%	93.8%	93.8%	93.5%	93.3%	92.9%	92.5%	92.2%	91.8%	91.4%	
Pressure ratio	-	-1.5	1.3	4.4	4.4	7.9	11.9	16.4	21.7	27.8	34.7	42.5	
Condenser glide	K	6.8	6.8	6.9	6.9	7.0	7.1	7.3	7.4	7.6	7.9	8.1	
Evaporator glide	K	0.4	0.4	0.4	0.4	0.3	0.2	0.2	0.2	0.3	0.4	0.4	
Condensing pressure	bar	0.2	0.2	0.1	0.1	0.1	0.1	0.2	0.4	0.6	0.6	0.5	
Evaporating pressure	bar	7.23	7.41	7.56	7.56	7.68	7.75	7.79	7.78	7.71	7.60	7.42	
COP	-	1.07	1.08	1.09	1.09	1.10	1.09	1.07	1.04	1.01	0.96	0.91	
Discharge temperature	°C	2.27	2.26	2.26	2.26	2.25	2.25	2.24	2.23	2.22	2.21	2.20	
Volumetric capacity	kJ/m <sup>3</sup>	9.9	12.7	15.8	15.8	19.3	23.3	27.8	33.1	39.2	46.1	53.9	
		806	824	839	839	849	854	853	845	831	812	786	

Table 16

	Quantity	Units
R744	Capacity relative to reference	
R23R1132	COP relative to reference	
a	Discharge temperature difference (K)	
	Pressure ratio	-
	Condenser glide	K
	Evaporator glide	K
	Condensing pressure	bar
	Evaporating pressure	bar
	COP	-
	Discharge temperature	°C
	Volumetric capacity	kJ/m <sup>3</sup>

Table 17

Quantity	Units												
		R744	12%	12%	12%	12%	12%	12%	12%	12%	12%	12%	12%
Capacity relative to reference													
COP relative to reference		R23	0%	10%	20%	30%	40%	48%	58%	68%	78%	88%	98%
Discharge temperature difference (K)		R1132a	88%	78%	68%	58%	48%	38%	28%	18%	8%	8%	8%
Pressure ratio	-		91.4%	93.3%	94.6%	95.5%	95.7%	95.2%	94.0%	92.2%	89.8%		
Condenser glide	K		94.0%	93.8%	93.6%	93.3%	92.9%	92.5%	92.1%	91.7%	91.3%		
Evaporator glide	K		3.2	6.2	9.6	13.5	18.0	23.2	29.2	36.0	43.9		
Condensing pressure	bar		6.8	6.9	7.0	7.1	7.2	7.4	7.6	7.8	8.0		
Evaporating pressure	bar		0.9	0.8	0.7	0.6	0.5	0.5	0.5	0.6	0.7		
COP	-		0.4	0.3	0.2	0.2	0.3	0.4	0.6	0.7	0.7		
Discharge temperature	°C		7.65	7.82	7.95	8.05	8.12	8.13	8.10	8.01	7.87		
Volumetric capacity	kJ/m <sup>3</sup>		1.12	1.13	1.14	1.14	1.13	1.10	1.07	1.03	0.98		
			2.27	2.26	2.26	2.25	2.24	2.23	2.22	2.21	2.20		
			14.6	17.6	21.0	24.9	29.4	34.6	40.6	47.4	55.3		
			855	872	885	893	894	890	879	862	839		

Table 18

Quantity	Units										
		R744	16%	16%	16%	16%	16%	16%	16%	16%	16%
		R23	0%	10%	20%	30%	40%	50%	60%	70%	
		R1132a	84%	74%	64%	54%	44%	34%	24%	14%	
Capacity relative to reference			93.9%	95.6%	96.9%	97.6%	97.6%	96.9%	95.6%	93.6%	
COP relative to reference			94.0%	93.7%	93.5%	93.1%	92.8%	92.3%	91.9%	91.4%	
Discharge temperature difference (K)			5.5	8.7	12.3	16.5	21.2	26.8	33.1	40.4	
Pressure ratio	-		6.9	6.9	7.0	7.1	7.3	7.4	7.6	7.8	
Condenser glide	K		1.0	0.9	0.8	0.6	0.6	0.5	0.6	0.7	
Evaporator glide	K		0.4	0.3	0.3	0.3	0.3	0.5	0.7	0.8	
Condensing pressure	bar		7.85	8.01	8.14	8.23	8.28	8.29	8.24	8.14	
Evaporating pressure	bar		1.15	1.16	1.16	1.16	1.14	1.12	1.08	1.04	
COP	-		2.26	2.26	2.25	2.24	2.24	2.22	2.21	2.20	
Discharge temperature	°C		16.9	20.1	23.7	27.9	32.6	38.2	44.5	51.8	
Volumetric capacity	kJ/m <sup>3</sup>		878	894	906	912	913	906	894	876	

**[0107]** This data shows that ternary compositions of R-1132a, R23 and carbon dioxide are suitable as drop-in replacements for R-508 compositions. In particular it is noted that compositions including about 20 to about 60% by weight R-23 provide for both an optimised capacity, which when combined with flammability reducing characteristics of R-23 may be particularly desirable.

**[0108]** Preferences and options for a given aspect, feature or parameter of the invention should, unless the context indicates otherwise, be regarded as having been disclosed in combination with any and all preferences and options for all other aspects, features and parameters of the invention.

**[0109]** The invention is defined by the following claims.

## Claims

1. A composition comprising:

- i) 1,1-difluoroethene (vinylidene fluoride, R-1132a);
- ii) trifluoromethane (R-23); and
- iii) 1% by weight to 45% by weight carbon dioxide (R-744, CO<sub>2</sub>).

2. A composition according to claim 1 further comprising one or more compound selected from hexafluoroethane (R-116) and/or ethane (R-170).

3. A composition according to any of the preceding claims comprising from about 1 to about 98% by weight R-1132a and/or from about 1 to about 98% by weight R-23, wherein the term about means  $\pm 0.5$  % by weight.

4. A composition according to any the preceding claims comprising from 35 to 95% by weight R-1132a.

5. A composition according to any the preceding claims comprising up to about 80% by weight R-116, preferably from about 1 to 60% by weight R-116, wherein the term about means  $\pm 0.5$  % by weight.

6. A composition according to any of the preceding claims comprising up to 40% by weight R-170, preferably from 1 to 30% by weight R-170.

7. A composition according to any of the preceding comprising from about 1 to 30% by weight carbon dioxide, preferably from 1 to 15% by weight carbon dioxide.

8. A composition according to any preceding claim comprising 35 to 98% by weight R-1132a, 1 to 60% by weight R-23 and 1 to 20% by weight carbon dioxide, more preferably comprising 40 to 60% by weight R-23; wherein the composition does not additionally comprise hexafluoroethane (R-116).

9. A composition according to claims or 8 comprising 4 to 16% by weight carbon dioxide.

10. A composition according to any of the preceding claims, wherein the composition is less flammable than R-1132a alone, wherein the composition has:

- a. a higher flammable limit when measured according to the methods specified by ASHRAE-34;
- b. a higher ignition energy when determined in a 500ml glass flask by the method of ASTM E659-78; and/or
- c. a lower flame velocity 20 compared to R-1132a alone.

11. A composition according to any of the preceding claims which is non-flammable, preferably wherein the composition is non-flammable at ambient temperature, preferably wherein the composition is non-flammable at 60 °C.

12. A composition according to any of the preceding claims which has a temperature glide in an evaporator or condenser of less than about 10 K, preferably less than about 5 K; and/or which has a critical temperature of greater than about 0 °C, preferably greater than about 10 °C; and/or whose volumetric refrigeration capacity is at least 90% of that of R-508 at comparable cycle conditions; and/or whose compressor discharge temperature is within 15 K of that of R-508 at comparable cycle conditions.

13. A composition comprising a lubricant, and/or a stabiliser, and/or flame retardant, and a composition according to

any of the preceding claims.

14. A heat transfer device containing a composition as defined in any one of claims 1 to 13, wherein the heat transfer device is a refrigeration device, more preferably wherein the heat transfer device comprises an ultra-low temperature refrigeration system.

## Patentansprüche

1. Zusammensetzung, die Folgendes umfasst:

- i) 1,1-Difluorethen (Vinylidenfluorid, R-1132a);
- ii) Trifluormethan (R-23); und
- iii) 1 Gew.-% bis 45 Gew.-% Kohlendioxid (R-744, CO<sub>2</sub>).

2. Zusammensetzung nach Anspruch 1, die ferner eine oder mehrere Verbindungen umfasst, die aus Hexafluorethan (R-116) und/oder Ethan (R-170) ausgewählt sind.

3. Zusammensetzung nach einem der vorhergehenden Ansprüche, die von etwa 1 bis etwa 98 Gew.-% R-1132a und/oder von etwa 1 bis etwa 98 Gew.-% R-23 umfasst, wobei der Ausdruck "etwa"  $\pm 0,5$  Gew.-% bedeutet.

4. Zusammensetzung nach einem der vorhergehenden Ansprüche, die von 35 bis 95 Gew.-% R-1132a umfasst.

5. Zusammensetzung nach einem der vorhergehenden Ansprüche, die bis zu etwa 80 Gew.-% R-116, bevorzugt von etwa 1 bis 60 Gew.-% R-116, umfasst, wobei der Ausdruck "etwa"  $\pm 0,5$  Gew.-% bedeutet.

6. Zusammensetzung nach einem der vorhergehenden Ansprüche, die bis zu 40 Gew.-% R-170, bevorzugt von 1 bis 30 Gew.-% R-170, umfasst.

7. Zusammensetzung nach einem der vorhergehenden Ansprüche, die von etwa 1 bis 30 Gew.-% Kohlendioxid, bevorzugt von 1 bis 15 Gew.-% Kohlendioxid, umfasst.

8. Zusammensetzung nach einem vorhergehenden Anspruch, die 35 bis 98 Gew.-% R-1132a, 1 bis 60 Gew.-% R-23 und 1 bis 20 Gew.-% Kohlendioxid umfasst, stärker bevorzugt 40 bis 60 Gew.-% R-23 umfasst; wobei die Zusammensetzung nicht zusätzlich Hexafluorethan (R-116) umfasst.

9. Zusammensetzung nach den Ansprüchen 7 oder 8, die 4 bis 16 Gew.-% Kohlendioxid umfasst.

10. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei die Zusammensetzung weniger entflammbar als R-1132a allein ist, wobei die Zusammensetzung Folgendes aufweist:

- a. eine höhere Entflammbarkeitsgrenze, wenn nach den durch ASH RAE-34 spezifizierten Verfahren gemessen wird;
- b. eine höhere Zündenergie, wenn in einem 500 ml Glaskolben durch das Verfahren von ASTM E659-78 bestimmt wird; und/oder
- c. eine niedrigere Flammgeschwindigkeit 20 im Vergleich zu R-1132a allein.

11. Zusammensetzung nach einem der vorhergehenden Ansprüche, die nicht entflammbar ist, bevorzugt wobei die Zusammensetzung bei Umgebungstemperatur nicht entflammbar ist, bevorzugt wobei die Zusammensetzung bei 60 °C nicht entflammbar ist.

12. Zusammensetzung nach einem der vorhergehenden Ansprüche, die ein Temperatursleit in einem Verdampfer oder einem Kondensator von unter etwa 10 K, bevorzugt unter etwa 5 K, aufweist; und/oder die eine kritische Temperatur von über etwa 0 °C, bevorzugt über etwa 10 °C, aufweist; und/oder deren volumetrische Kühlkapazität bei vergleichbaren Zyklusbedingungen wenigstens 90 % von der von R-508 beträgt; und/oder deren Kompressorauflasttemperatur bei vergleichbaren Zyklusbedingungen innerhalb von 15 K von der von R-508 liegt.

13. Zusammensetzung, die ein Schmiermittel und/oder einen Stabilisator und/oder ein Flammschutzmittel und eine Zusammensetzung nach einem der vorhergehenden Ansprüche umfasst.
14. Wärmeübertragungsvorrichtung, die eine Zusammensetzung enthält, wie in einem der Ansprüche 1 bis 13 definiert, wobei die Wärmeübertragungsvorrichtung eine Kühlvorrichtung ist, stärker bevorzugt wobei die Wärmeübertragungsvorrichtung ein Ultraniedrigtemperatur-Kühlsystem umfasst.

## Revendications

1. Composition comprenant :

- i) du 1,1-difluoroéthylène (fluorure de vinylidène, R-1132a) ;
- ii) du trifluorométhane (R-23) ; et
- iii) 1 % en poids à 45 % en poids de dioxyde de carbone (R-744, CO<sub>2</sub>).

2. Composition selon la revendication 1, comprenant en outre un ou plusieurs composés choisis parmi l'hexafluoroéthane (R-116) et/ou l'éthane (R-170).

3. Composition selon l'une quelconque des revendications précédentes, comprenant d'environ 1 à environ 98 % en poids de R-1132a et/ou d'environ 1 à environ 98 % en poids de R-23, le terme « environ » désignant  $\pm 0,5$  % en poids.

4. Composition selon l'une quelconque des revendications précédentes comprenant de 35 à 95 % en poids de R-1132a.

5. Composition selon l'une quelconque des revendications précédentes, comprenant jusqu'à environ 80 % en poids de R-116, de préférence d'environ 1 à 60 % en poids de R-116, le terme « environ » désignant  $\pm 0,5$  % en poids.

6. Composition selon l'une quelconque des revendications précédentes, comprenant jusqu'à 40 % en poids de R-170, de préférence de 1 à 30 % en poids de R-170.

7. Composition selon l'une quelconque des revendications précédentes, comprenant d'environ 1 à 30 % en poids de dioxyde de carbone, de préférence de 1 à 15 % en poids de dioxyde de carbone.

8. Composition selon l'une quelconque des revendications précédentes, comprenant 35 à 98 % en poids de R-1132a, 1 à 60 % en poids de R-23 et 1 à 20 % en poids de dioxyde de carbone, comprenant de préférence 40 à 60 % en poids de R-23 ;  
la composition ne comprenant pas d'hexafluoroéthane (R-116) en plus.

9. Composition selon les revendications 7 ou 8 comprenant 4 à 16 % en poids de dioxyde de carbone.

10. Composition selon l'une quelconque des revendications précédentes, la composition étant moins inflammable que le R-1132a seul, la composition ayant :

- a. une limite d'inflammabilité supérieure lorsqu'elle est mesurée selon les procédés spécifiés par la norme ASHRAE-34 ;
- b. une énergie d'inflammation plus élevée lorsqu'elle est déterminée dans un ballon en verre de 500 ml par le procédé de la norme ASTM E659-78 ; et/ou
- c. une vitesse de la flamme inférieure 20 par rapport au R-1132a seul.

11. Composition selon l'une quelconque des revendications précédentes, qui est non-inflammable, de préférence la composition étant non-inflammable à température ambiante, de préférence la composition étant non-inflammable à 60 °C.

12. Composition selon l'une quelconque des revendications précédentes, qui a une température de glissement dans un évaporateur ou un condenseur inférieure à environ 10 K, de préférence inférieure à environ 5 K ; et/ou qui a une température critique supérieure à environ 0 °C, de préférence supérieure à environ 10 °C ; et/ou dont la capacité de réfrigération volumétrique est d'au moins 90 % de celle du R-508 dans des conditions de cycle comparables ; et/ou

dont la température de refoulement du compresseur est inférieure ou égale à 15 K de celle du R-508 dans des conditions de cycle comparables.

5 13. Composition comprenant un lubrifiant, et/ou un stabilisant, et/ou un ignifuge, et une composition selon l'une quelconque des revendications précédentes.

10 14. Dispositif de transfert de chaleur contenant une composition telle que définie dans l'une quelconque des revendications 1 à 13,  
le dispositif de transfert de chaleur étant un dispositif de réfrigération, plus préférablement le dispositif de transfert de chaleur comprenant un système de réfrigération à très basse température.

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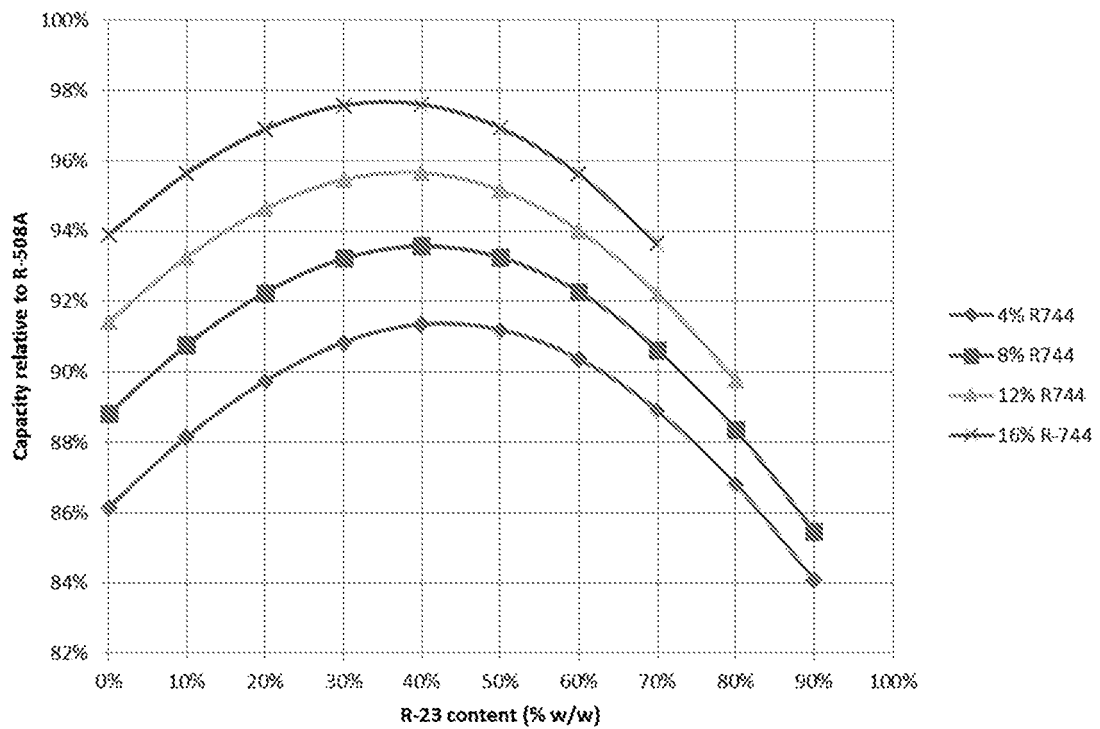
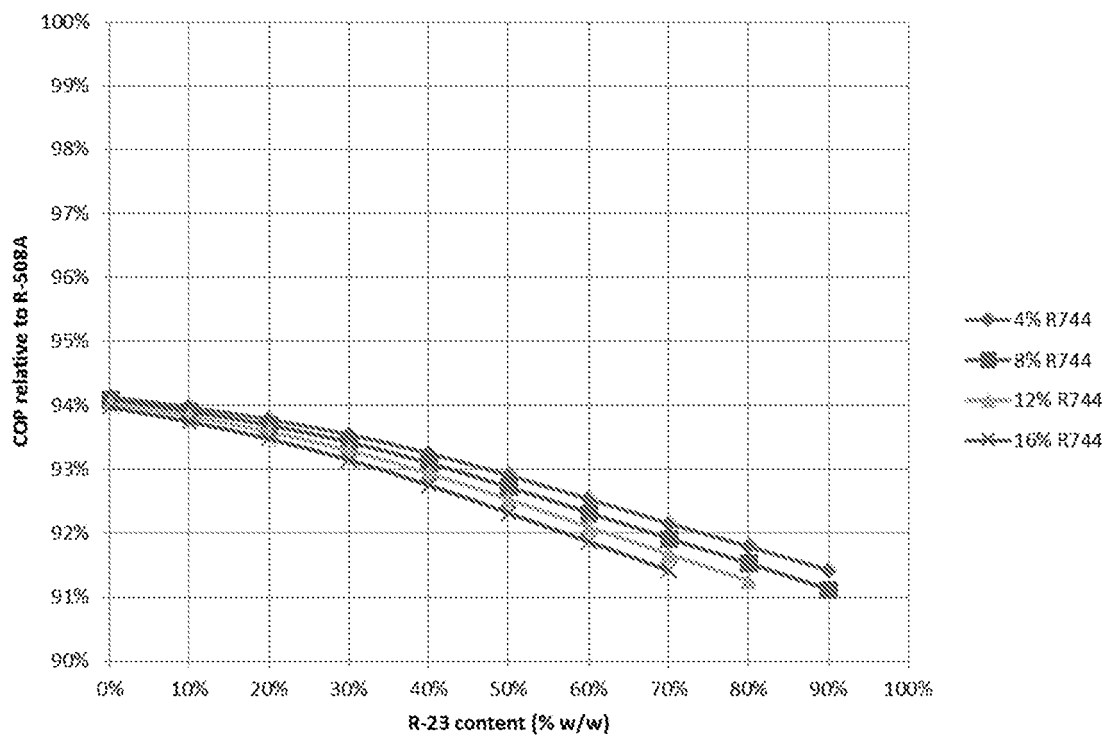
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**Figure 1 Capacity of R744/R23/R1132a mixtures****Figure 2 - COP of R744/R23/R1132a mixtures**

## REFERENCES CITED IN THE DESCRIPTION

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